a M → L charge-transfer transition on the basis of its intensity and the shift to lower energy on going from $Mo(pic)_4$ to the more easily oxidizable $W(pic)_4$ complex, for which M → L charge transfer has been shown previously.[1] Analogous to $W(pic)_4$, the low-energy band of $Mo(pic)_4$ exhibits shifts to higher energy in more polar and/or protic solvents: $CH_3COOH$ (21 800 $cm^{-1}$), $H_2O$ (22 300 $cm^{-1}$). The 90-MHz $^1H$ NMR spectrum of $Mo(pic)_4$ in $CD_2Cl_2$ at 35 °C consists of a poorly resolved doublet at 9.84 ppm (downfield from $Me_4Si$) and a multiplet centered at 7.71 ppm. The doublet is assigned to the proton $\alpha$ to the pyridine nitrogen, while the remaining aromatic protons cause the multiplet. The $^1H$ NMR spectrum of the $W(pic)_4$ complex exhibits the same pattern.[1]

Attempts to oxidize $Mo(pic)_4$ to the $d^1$ $Mo(pic)_4^+$ cation with either $Cl_2$ or $Br_2$ for up to several hours yielded only unreacted $Mo(pic)_4$. Such oxidations can be accomplished for the $W(pic)_4$[1] and $W(q_4)$[3] complexes, where $q^-$ = 8-quinolinolato. A variety of substituted dithiocarbamato eight-coordinate molybdenum(IV) complexes have also been successfully oxidized to molybdenum(V) eight-coordinate cations by not only $Cl_2$ and $Br_2$ but also $I_2$.[4] After one attempt to oxidize the $Mo(pic)_4$ complex with a $Cl_2/CCl_4$ solution, the recovered complex after standing in a capped vial for over a week was observed to have turned blue. The infrared spectrum of this product has five bands between 960 and 860 $cm^{-1}$, consistent with the formation of a molybdenum–oxo complex.

The single-crystal x-ray structure determination of the tetrakis(5-bromo-8-quinolinolato)tungsten(IV) complex revealed it possesses $D_{2d}$ dodecahedral geometry.[5] The ligands span the *m* edges with the $\pi$-acceptor nitrogen atoms occupying the B sites and the $\pi$-donor phenolic oxygens occupying the A sites in accordance with Orgel's rule.[6] Given the chemical similarities between 8-quinolinol and picolinic acid, as well as their nearly equal bite sizes, it is assumed the $W(pic)_4$ and $Mo(pic)_4$ complexes also possess $D_{2d}$ (*mmmm*) dodecahedral geometry.

Only a handful of bidentate ligands have been reported to yield tetrakis eight-coordinate molybdenum(IV) complexes. These ligands include $CO_3^{2-}$,[7] $C_2O_4^{2-}$,[8] $S_2CR^-$,[9] $S_2CNR_2^-$,[4,10] and $(SCC_6H_5)_2CH^-$.[11,12] In addition, no concrete structural evidence is available for the molybdenum(IV) complexes reported for the $CO_3^{2-}$ and $C_2O_4^{2-}$ ligands.

The present results suggest more drastic reaction conditions are necessary to synthesize eight-coordinate molybdenum(IV) complexes than the analogous tungsten(IV) complexes, when oxidation, as well as substitution, is occurring at the metal center. This trend is consistent with the relative oxidation-state stabilities of molybdenum and tungsten. In general, tungsten favors higher oxidation states.

**Acknowledgment.** We thank the Materials Research Laboratory of the University of Massachusetts for partial support of this research. We also wish to acknowledge microanalyses done by the University of Massachusetts Microanalytical Laboratory.

**Registry No.** $Mo(pic)_4$, 66008-11-5; $Mo(CO)_6$, 13939-06-5.

## References and Notes

(1) C. J. Donahue and R. D. Archer, *Inorg. Chem.*, **16**, 2903 (1977); cf. Abstracts, 169th National Meeting of the American Chemical Society, Philadelphia, Pa., 1975, No. INOR 56.
(2) T. E. Dorsett and R. A. Walton, *J. Chem. Soc., Dalton Trans.*, 347 (1976).
(3) R. D. Archer, W. D. Bonds, Jr., and R. A. Pribush, *Inorg. Chem.*, **11**, 1550 (1972).
(4) (a) A. Nieuwpoort, H. M. Glaessen, and J. G. M. van der Linden, *Inorg. Nucl. Chem. Lett.*, **11**, 869 (1975); (b) A. Nieuwpoort, *J. Less-Common Met.*, **36**, 271 (1974); (c) J. C. Wijnhoven, *Cryst. Struct. Commun.*, **2**, 637 (1973); (d) Z. B. Varadi and A. Nieuwpoort, *Inorg. Nucl. Chem. Lett.*, **10**, 801 (1974); (e) A. Nieuwpoort, J. H. F. Moonen, and J. A. Cras, *Rel. Trav. Chim. Pays-Bas*, **92**, 1086 (1973).
(5) W. D. Bonds, Jr., R. D. Archer, and W. C. Hamilton, *Inorg. Chem.*, **10**, 1764 (1971).
(6) L. E. Orgel, *J. Inorg. Nucl. Chem.*, **14**, 136 (1960).
(7) M. C. Steele, *Aust. J. Chem.*, **10**, 367 (1957).
(8) M. C. Steele, *Aust. J. Chem.*, **10**, 368 (1957).
(9) M. Bonamico, C. Dessy, V. Fares, D. Porta, and L. Scaramuzza, *Chem. Commun.*, 365 (1971); M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *Cryst. Struct. Commun.*, **1**, 91 (1972); M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J. Chem. Soc., Dalton Trans.*, 1258 (1974).
(10) D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1152 (1969); D. C. Bradley and M. H. Gitlitz, *Chem. Commun.*, 289 (1965); T. M. Brown and J. N. Smith, *J. Chem. Soc., Dalton Trans.*, 1614 (1972); J. N. Smith and T. M. Brown, *Inorg. Nucl. Chem. Lett.*, **6**, 441 (1970).
(11) E. Uhlemann and U. Eckelmann, *Z. Chem.*, **12**, 298 (1972).
(12) D. C. Bradley and I. F. Rendall have unpublished evidence for the 8-quinolinolato complex, too.

---

Contribution from the Department of Chemistry,
The University of Nebraska—Lincoln, Lincoln, Nebraska 68588

## A Direct One-Step Preparation of Bis(dinitrogen) Complexes of Molybdenum(0) from Molybdenum(V) Chloride

T. Adrian George* and Mark E. Noble[1]

*Received October 11, 1977*

Bis(dinitrogen) complexes of molybdenum(0) have found extensive use in the study of the chemistry of the coordinated dinitrogen ligand, with possible relevance to nitrogenase enzyme systems.[2] The complexes studied generally contain organophosphines as coligands, most notably 1,2-bis(diphenylphosphino)ethane (DPPE), and several schemes have been developed for their synthesis. Hidai et al. were the first to report dinitrogenmolybdenum(0) complexes,[3] the synthesis of which involved the triethylaluminum reduction of molybdenum(III) acetylacetonate in the presence of the appropriate phosphine and under a $N_2$ atmosphere. The reaction schemes used required several days for completion and only small yields of product were obtained. Chatt and co-workers have employed the magnesium metal or sodium amalgam reduction of $MoCl_3(THF)_3$ in the presence of organophosphines and under $N_2$.[4] The molybdenum(III) reactant is itself prepared in several steps from $[MoCl_5]_2$. Aresta and Sacco have described the synthesis of $[Mo(N_2)_2L_4]$ complexes (L = monodentate phosphine) from the sodium powder reduction of $[MoCl_4L_2]$.[5] George and Seibold previously reported obtaining $[Mo(N_2)_2L_4]$ and $[Mo(N_2)_2L'_2]$ complexes (L′ = bidentate phosphine) from the sodium amalgam reduction of $[MoCl_4L_2]$ and $[MoCl_4L']$, the molybdenum(IV) reactants having been prepared from $[MoCl_5]_2$.[6] The present note deals with the direct synthesis from $[MoCl_5]_2$ in good yields of complexes of the type $[Mo(N_2)_2L_4]$ and $[Mo(N_2)_2L'_2]$, where L = $Ph_2PCH_3$ and L′ = DPPE, 1,2-bis(diethylphosphino)ethane (DEPE), and 1-diphenylarsino-2-diphenylphosphinoethane (ARPHOS).

### Experimental Section

All solvents were reagent grade and were dried, distilled, and deaerated under dinitrogen prior to use, using the following drying agents during distillation: THF, sodium benzophenone; benzene, calcium hydride; methanol, magnesium methoxide. Molybdenum pentachloride and DPPE were used as obtained from Research Organic/Inorganic Chemicals, Inc. ARPHOS and $Ph_2PCH_3$ were used as obtained from Pressure Chemical Co. and Strem Chemicals, Inc., respectively. DEPE, from OrgMet, Inc., was purified by vacuum distillation before use. Operations were conducted in a glovebag under a dinitrogen atmosphere. Product identification was based on the characteristic infrared spectra of the compounds as obtained on a Perkin-Elmer Model 621 spectrophotometer as KBr disks. Nitrogen content was determined by the measurement of the gas evolved by thermal or a combination of thermal and bromine decomposition.

© 1978 American Chemical Society

**Preparation of $Mo(N_2)_2(DPPE)_2$ (1).** DPPE (8.81 g, 22.1 mmol) and 250 mL of THF were combined in a round-bottom flask equipped with $N_2$ inlet and magnetic stirrer. $[MoCl_5]_2$ (2.52 g, 9.22 mmol of Mo(V)) was added to produce a brown suspension, followed by the addition of 1% Na/Hg (425 g, 185 mmol of Na). After stirring 16 h, the THF slurry was decanted, filtered over Celite, and washed through with 200 mL of benzene. Solvent was then removed using a rotary evaporator. The orange-brown residue was dissolved in 150 mL of benzene, followed again by Celite filtration and rinsing with 100 mL of benzene. Product was precipitated by the addition of 400 mL of methanol, collected by filtration, washed with methanol, and dried in vacuo. The bright orange product weighed 4.60 g (53% yield). Anal. Calcd for $MoN_4C_{52}H_{48}P_4$: N, 5.9. Found: N, 5.8. $\nu_{N\equiv N}$ 1978 $cm^{-1}$ (vs).

**Preparation of $Mo(N_2)_2(DEPE)_2$.** DEPE (0.744 g, 3.61 mmol), 50 mL of THF, $[MoCl_5]_2$ (0.410 g, 1.50 mmol of Mo(V)), and 1% Na/Hg (69 g, 30 mmol of Na) were combined as above and stirred for 10 h. The reaction mixture was then decanted, Celite filtered, and washed through with 40 mL of benzene. After rotary evaporation of solvent, the residue was dissolved in 10 mL of benzene. This was filtered and rinsed with 20 mL of benzene. Methanol (60 mL) was added to the dark orange filtrate to precipitate product which was collected by filtration, washed with methanol, and dried in vacuo. The bright orange crystals weighed 0.415 g (49% yield). Anal. Calcd for $MoN_4C_{20}H_{48}P_4$: N, 9.9. Found: N, 9.6. $\nu_{N\equiv N}$ 1927 $cm^{-1}$ (vs).

**Preparation of $Mo(N_2)_2(ARPHOS)_2$.** ARPHOS (4.70 g, 10.6 mmol), 125 mL of THF, $[MoCl_5]_2$ (1.21 g, 4.43 mmol of Mo(V)), and 1% Na/Hg (200 g, 87 mmol of Na) were combined as for compound **1** and stirred for 16 h. The THF slurry was decanted, Celite filtered, and rinsed through with 160 mL of benzene. Solvent was removed using a rotary evaporator, leaving an orange-brown residue to which 75 mL of benzene was then added. This was filtered over Celite and rinsed through with 90 mL of benzene. Methanol (250 mL) was added to precipitate product which was collected by filtration, washed with methanol, and then dried in vacuo. The yellow-orange product weighed 2.10 g (46% yield). Anal. Calcd for $MoN_4C_{52}H_{48}As_2P_2$: N, 5.4. Found: N, 4.8. $\nu_{N\equiv N}$ 1952 $cm^{-1}$ (vs).

**Preparation of $Mo(N_2)_2(Ph_2PCH_3)_4$.** $Ph_2PCH_3$ (1.22 g, 6.09 mmol), 50 mL of THF, $[MoCl_5]_2$ (0.416 g, 1.52 mmol of Mo(V)), and 1% Na/Hg (70 g, 30 mmol of Na) were combined as for compound **1** and stirred 10 h. The THF slurry was then decanted, filtered over Celite, and rinsed through with 50 mL of benzene. Solvent was removed using a rotary evaporator, leaving a deep orange-red oil to which 20 mL of benzene was added. This was then Celite filtered and washed through with 30 mL of benzene. Ice-chilled methanol (100 mL) was then added, followed by further chilling (0 °C) of the resulting mixture. Product was collected by filtration, washed with methanol, and dried in vacuo. The orange-red crystals weighed 0.779 g (54% yield). Anal. Calcd for $MoN_4C_{52}H_{52}P_4$: N, 5.9. Found: N, 5.9. $\nu_{N\equiv N}$ 1922 $cm^{-1}$ (vs).

## Results and Discussion

The reduction of molybdenum(V) chloride in the presence of $N_2$ and a suitable phosphine ligand using sodium amalgam and THF as solvent has proven to be a very convenient route to the synthesis of bis(dinitrogen)molybdenum(0) complexes. The reaction proceeds readily and has provided good yields for the organophosphines employed.

The yields have been found to be dependent on the purity of the reactant materials. The highest yield obtained for compound **1** was 72% and involved the use of molybdenum(V) chloride purified by sublimation.[7] Yield was also found to increase when DPPE, recrystallized from benzene–methanol in order to remove phosphoryl species, was employed. Since small amounts of impurities do not appreciably affect the yield, purification of reactants is not employed for routine syntheses.[8]

Yields were found to be virtually unaffected by the amount of stirring time allowed for reaction. Reaction times varying from 3 to 47 h have been studied for compound **1** and have been found to produce no significant difference in yields. Thus, the reaction appears complete after only several hours of stirring.

The addition of molybdenum(V) chloride to the THF solvent prior to the addition of any organophosphine has been found in the three trials thus conducted to cause solvent polymerization as evidenced by an intense infrared absorption for the reaction mixture at 1111 $cm^{-1}$. This absorption was absent in the spectra of those reaction mixtures containing dissolved phosphines prior to the addition of the molybdenum(V) chloride. Although product was formed in the presence of the polymer as indicated by the N–N absorption also in the spectra of the reaction mixture, the polymer prevented isolation of the product by the standard procedures employed for the complex containing $Ph_2PCH_3$ as coligand. The proper order of addition of reactants is therefore essential for facile workup.

Reactions using DPPE as coligand have been found to involve the formation of small quantities of $[MoH_4(DPPE)_2]$ in a competing process, the hydrogen source presumably arising from solvent decomposition. The tetrahydride can coprecipitate with the bis(dinitrogen) complex when higher methanol/benzene solution ratios or when chilling of the precipitating liquor are employed. Pure bis(dinitrogen) product can be obtained, however, by proper design of the final crystallization (see Experimental Section).

With the use of the presently described synthetic scheme, it is hoped that the study of dinitrogenmolybdenum(0) complexes will be facilitated.

**Acknowledgment.** We are grateful to the National Science Foundation for support of this work through Grant No. CHE76-80878. We also thank Drs. John W. McDonald and William E. Newton of the Charles F. Kettering Research Laboratory for helpful discussions.

**Registry No.** $Mo(N_2)_2(DPPE)_2$, 41700-58-7; $Mo(N_2)_2(DEPE)_2$, 66008-10-4; $Mo(N_2)_2(ARPHOS)_2$, 37138-36-6; $Mo(N_2)_2(Ph_2PCH_3)_4$, 66008-09-1; $[MoCl_5]_2$, 26814-39-1.

## References and Notes

(1) Avery Fellow (1976–1980).
(2) See, for example, E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 160 (1977).
(3) M. Hidai, K. Tominari, Y. Uchida, and A. Misono, *Chem. Commun.*, 814 (1969); M. Hidai, K. Tominari, and Y. Uchida, *ibid.*, 1392 (1969); *J. Am. Chem. Soc.*, **94**, 110 (1972).
(4) J. Chatt and A. G. Webb, *J. Organomet. Chem.*, **27**, C15 (1971); J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 2074 (1975).
(5) M. Aresta and A. Sacco, *Gazz. Chim. Ital.*, **102**, 755 (1972).
(6) T. A. George and C. D. Seibold, *Inorg. Chem.*, **12**, 2544 (1973).
(7) R. Colton and I. B. Tomkins, *Aust. J. Chem.*, **18**, 447 (1965).
(8) The 72% yield for compound **1** was obtained on a small-scale synthesis (1.5 mmol of Mo(V)). For three reactions conducted on such a scale using the same sample of purified molybdenum(V) chloride, yields varied from 66 to 72%. Using unpurified $[MoCl_5]_2$ on the same scale, a 62% yield was obtained. Smaller yields have been generally found for larger scale syntheses (see Experimental Section).

---

Contribution from the Department of Chemistry,
University of Texas at Austin, Austin, Texas 78712

# (Trifluoromethyl)sulfur Trifluoride. An Improved Synthesis, New NMR Data, and Stereochemistry

R. W. Braun, A. H. Cowley,* M. C. Cushner, and R. J. Lagow*

*Received December 29, 1977*

(Trifluoromethyl)sulfur trifluoride has been prepared by the action of $F_2$ or oxidative fluorinating agents on $CS_2$, $CF_3SCl$, or $(CF_3S)_2CS$.[1] However, the commercial availability of $CF_3SSCF_3$ renders this compound an ideal starting point for the one-step synthesis of $CF_3SF_3$. The conversion $CF_3SSCF_3 \rightarrow 2CF_3SF_3$ has, in fact, been accomplished previously by treatment with $CF_3OF$,[1c] $ClF_3$,[2] or $F_2$.[1c] However, the $CF_3OF$ and $ClF_3$ reactions are difficult to control, and the direct fluorination involved a labor intensive batchwise method. The

© 1978 American Chemical Society